

DECLARATION

I, Mizuho UTAFUSA, a subject of Japan residing at 1192, Noguwa ,  
Kamigori-cho, Ako-gun, Hyogo 678-1202, Japan, solemnly and sincerely  
declare:

That I have a thorough knowledge of the Japanese and English  
languages; and

That the attached pages contain a correct translation into  
English of the priority document of Japanese Patent Application No.  
11940/2003.

Signed this 1st day of July, 2008

歌房みずほ

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Mizuho UTAFUSA

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**【Document】 Specification**

**【Title】** HEAT-SHRINKABLE TRANSLUCENT WHITE FILM, SHRINK LABEL AND CONTAINER WITH LABEL

**【Field of the Invention】****【0001】**

The present invention relates to a heat-shrinkable opaque white (translucent white) film which is impervious to light, a shrink label prepared from the heat-shrinkable opaque white film, and a labeled container including a container body and the label applied to the container body by heat shrinkage.

**【Description of the Related Art】****【0002】**

Alcoholic beverages such as beer, sake, and wine, green tea, and beverages containing vitamins are susceptible to discoloration and/or deterioration caused by light. Widely used containers typically for beverages susceptible to light-induced deterioration are plastic bottles and glass bottles which are colored for achieving imperviousness to light. These colored containers contain colorants, and this significantly inhibits recovery and reuse of used containers.

**【0003】**

A proposed solution to this is labeled containers including a colorless, transparent plastic bottle or glass bottle as a container body coated with a shrink label having imperviousness to light. Japanese Unexamined Patent Application Publication (JP-A) No. 2002-68202, for example, discloses a bottle having a heat-shrinkable synthetic resin film containing an ultraviolet screening agent such as zinc oxide. JP-A No. 2002-285020 discloses a container with a heat-shrinkable label prepared from a white film containing a specific amount of titanium dioxide. These containers, however, have relatively high light transmission factor particularly to visible light and do not have sufficient imperviousness to light. JP-A No. 2003-26252 discloses a container with a shrink label. The shrink label includes a heat-shrinkable film containing a white pigment and having one side to be designed and the other side printed black. This type of container, however, has a black inner side of the label, and when one look in on a beverage such as milk beverage or beer at an inlet of the container bottle, the beverage looks blackish and has poor appearance which could deteriorate one's appetite.

**【0004】**

**【Document 1】** Japanese Unexamined Patent Application Publication (JP-A) No. 2002-68202

**【Document 2】** Japanese Unexamined Patent Application Publication (JP-A) No. 2002-285020

**【Document 3】** Japanese Unexamined Patent Application Publication (JP-A) No. 2003-26252

**【Detailed Description of the Invention】****【Object of the Invention】****【0005】**

Accordingly, an object of the present invention is to provide a labeled container that can have sufficient imperviousness to light, can be printed clearly typically with a design, and yields an excellent appearance of the contents when viewed from outside. Another object of the present invention is to provide a heat-shrinkable opaque white film and a shrink label which are useful for preparing the labeled container

**【Aspects of the Invention】****【0006】**

After intensive investigations to achieve the above objects, the present inventors have found that, by covering a container body with a shrink label using a heat-shrinkable opaque white film having a specific layer configuration, the resulting container can have sufficient imperviousness to light, for example, a clear design, and show such an excellent appearance of the contents such as beverages that the contents look their original colors without discomfort. The present invention has been achieved based on these findings.

**【Advantages in the Invention】****【0007】**

Specifically, the present invention provides a heat-shrinkable opaque white film comprising a black core layer; and white back and front layers.

**【0008】**

The present invention also provides a shrink label comprising the heat-shrinkable opaque white film, and a preprinted ink label layer arranged on or above a surface of the front layer of the film.

**【0009】**

The present invention further provides a labeled container comprising a container body; and the shrink label arranged on or above the container body.

**【Embodiments】****【0010】**

The present invention will be illustrated in detail with reference to the attached drawings according to necessity. The heat-shrinkable opaque white film according to the present invention comprises a black core layer (central layer); and white back and front layers (front layer and back layer). The "front layer" means a layer which constitutes an outside layer when applied to a container and is to be printed typically with a design upon the preparation of a label. The "back layer" means a

layer lying near to a container when formed into a label. The heat-shrinkable opaque white film according to the present invention can have the black core layer, and has sufficient imperviousness to light. A design or such can be clearly printed when the film is formed into a label, since the front layer is white and the film is thereby opaque white. In addition, when the label is applied to a container to form a labeled container, the contents in the container, such as beverages, look natural without deterioration of their original colors when viewed from the spout of the container, since the back layer is white. The heat-shrinkable opaque white film may further comprise any other layer or layers within ranges not adversely affecting the properties such as heat-shrinkability, beauty and handleability, in addition to the core layer and the back and front layers. Examples of the other layers are transparent resin layers, other colored resin layers, and resin layers for improving adhesion between layers,

【0011】

The shrink label according to the present invention comprises the heat-shrinkable opaque white film and a preprinted ink label layer arranged on or above a surface of the front layer. FIG. 1 is a schematic cross-sectional view showing an example of the shrink label according to the present invention. The heat-shrinkable opaque white film 4 comprises a white front layer 1, a black core layer 2, and a white back layer 3. The preprinted ink label layer 5 is arranged on a surface of the front layer 1 of the film 4.

【0012】

Each of the front layer 1, the core layer 2, and the back layer 3 may independently comprise a heat-shrinkable film layer. Materials for such heat-shrinkable film layers can be those generally used as materials for heat-shrinkable films, such as polyester resins, polystyrene resins, polyolefin resins, and poly(vinyl chloride) resins. Each of these materials can be used alone or in combination.

【0013】

The polyester resins can be polyester resins prepared according to a conventional procedure such as condensation between a diol component and a dicarboxylic acid component (or a reactive derivative thereof). Examples of the diol component constituting the polyester resins are aliphatic diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, and 2,2,4-trimethyl-1,6-hexanediol; thiodiethanol; polyalkylene glycols such as diethylene glycol, dipropylene glycol, polyethylene glycol, and polypropylene glycol; alicyclic diols such as 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, and 1,4-cyclohexanedimethanol; and aromatic diols including ethylene oxide adducts of bisphenol compounds such as 2,2-bis(4'- $\beta$ -hydroxyethoxydiphenyl)propane and

bis(4'- $\beta$ -hydroxyethoxyphenyl)sulfone, as well as xylylene glycol. Each of these diol components can be used alone or in combination.

**【0014】**

Examples of the dicarboxylic acid component constituting the polyester resins are aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid; alicyclic dicarboxylic acids such as 1,4-decahydronaphthalenedicarboxylic acid, 1,5-decahydronaphthalenedicarboxylic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, and 1,4-cyclohexanedicarboxylic acid; and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 4,4'-biphenyldicarboxylic acid, trans-3,3'-stilbenedicarboxylic acid, trans-4,4'-stilbenedicarboxylic acid, 4,4'-dibenzoyldicarboxylic acid, and naphthalenedicarboxylic acids such as 2,6-naphthalenedicarboxylic acid. Each of these dicarboxylic acid components can be used alone or in combination.

**【0015】**

Preferred polyester resins are those prepared by using ethylene glycol as a main diol component, and an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, or a naphthalenedicarboxylic acid as a main dicarboxylic acid component.

**【0016】**

The polystyrene resins can be styrene-conjugated diene block copolymers such as styrene-butadiene-styrene block copolymers and styrene-isoprene-styrene block copolymers; and mixtures of the styrene-conjugated diene block copolymers with one or more other polymers such as polystyrenes or copolymers between styrene and an acrylic monomer such as (meth)acrylic ester. The styrene-conjugated diene block copolymers may each have a styrene content of about 30 to about 95 percent by weight and a conjugated diene content of about 5 to about 70 percent by weight.

**【0017】**

Each of the white front layer 1 and the white back layer 3 can independently comprise the resin component and a white colorant. Such white colorants are not limited and include white pigments such as titanium dioxide, antimony white, zinc sulfide, and zinc white. Among them, titanium dioxide is particularly preferred. The content of the white colorant in each of the front layer 1 and the back layer 3 can be set as appropriate according typically to the whiteness and cost and varies depending on the species of the white colorant. It is generally about 2 to about 30 percent by weight, and preferably about 3 to about 15 percent by weight of the total weight of each layer.

**【0018】**

The average particle diameter of a white pigment such as titanium dioxide, if used as the white colorant, is, for example, about 0.01 to about 1  $\mu\text{m}$ , preferably about 0.1 to about 0.5  $\mu\text{m}$ . If the average particle diameter is less than 0.01  $\mu\text{m}$ , dispersibility may be deteriorated. If it exceeds 1  $\mu\text{m}$ , the film may have a rough surface and show a deteriorated appearance.

**【0019】**

The black core layer 2 can comprise the resin component and a black colorant. The black colorant is not specifically limited and can be any of known black pigments, of which carbon black is typically preferred. The content of the black colorant in the black core layer 2 can be set as appropriate in consideration typically of the imperviousness to light and cost within ranges not adversely affecting the whiteness of the back and front layers of the film. It is generally 0.2 to 20 percent by weight, preferably 0.7 to 15 percent by weight based on the total volume of the core layer 2. The amount of the black colorant is preferably 0.05 percent by weight or more (e.g., about 0.05 to about 5 percent by weight) based on the total weight of the heat-shrinkable opaque white film. The content of the black colorant per unit area of the opaque white film is preferably  $1 \times 10^{-2} \text{ g/m}^2$  or more (e.g.,  $1 \times 10^{-2} \text{ g/m}^2$  to about  $5 \text{ g/m}^2$ ), and more preferably  $0.5 \text{ g/m}^2$  or more (e.g.,  $0.5 \text{ g/m}^2$  to about  $5 \text{ g/m}^2$ ).

**【0020】**

The average particle diameter of a black pigment such as carbon black, if used as the black colorant, is for example about 0.001 to about 10  $\mu\text{m}$ , and preferably about 0.01 to about 1  $\mu\text{m}$ . If the average particle diameter is less than 0.001  $\mu\text{m}$ , the dispersibility may often decrease. If it exceeds 10  $\mu\text{m}$ , it may be difficult to achieve sufficient imperviousness to light. Such a black core layer 2 can be a layer of dark grey color, prepared by adding a white colorant and the black colorant.

**【0021】**

It is not always necessary to use a transparent material as a resin material for constituting the core layer 2, since the core layer has the black color. Consequently, recycled materials such as failed printed films, borders on the periphery of films, and film pieces with printed portions can be effectively used as the resin material. This is a very economical advantage. In this case, the amount of the recycled material can be set as appropriate within ranges not adversely affecting properties such as imperviousness to light and heat-shrinkability and is generally preferably 30 percent by weight or less (e.g., about 1 to about 30 percent by weight) of the total amount of resin materials constituting the core layer 2.

**【0022】**

In the heat-shrinkable opaque white film 4 according to the present invention, it is not always

necessary to constitute all the front layer 1, the core layer 2 and the back layer 3 as heat-shrinkable film layers, as long as the heat-shrinkable opaque white film as a whole is heat-shrinkable. Heat-shrinkability can be imparted to the opaque white film 4, for example, by constituting one or two of the three layers as heat-shrinkable film layers, or arranging a heat-shrinkable film layer in addition to the three layers. Each of the front layer 1, the core layer 2, and the back layer 3 can comprise a printed layer or a coating layer, if not a heat-shrinkable film layer. The front layer 1 and the back layer 3 can be formed, for example, by printing both sides (back and front sides) of an black heat-shrinkable film layer to be the core layer 2 with an ink containing a white pigment such as titanium dioxide according to a conventional printing procedure such as gravure printing. Likewise, the core layer 2 can be formed by printing a white heat-shrinkable film layer to be the front layer 1 with an ink containing an black colorant according to a conventional printing procedure such as gravure printing. When the film comprise two or more heat-shrinkable film layers, resins constituting these layers may be of different species but are preferably of the same species from the viewpoints typically of workability and recycling property.

#### 【0023】

Representative layer configurations of the heat-shrinkable opaque white film 4 include (1) white heat-shrinkable film layer (front layer)/black heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer); (2) white heat-shrinkable film layer (front layer)/black heat-shrinkable film layer (core layer)/white preprinted layer (back layer); and (3) white preprinted layer (front layer)/black heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer). Preferred layer configurations in the present invention are those in which at least the core layer 2 is a black heat-shrinkable film layer. In these layer configurations, cost can be reduced. This is because, for example, a sufficient density can be achieved by directly kneading a black colorant into a resin. The black core layer can be formed by using a recycled material. When it is a black core layer, a larger amount of a recycled material can be used. It is preferred to constitute all the front layer 1, the core layer 2, and the back layer 3 as heat-shrinkable film layers. This is because, for example, if a printing process such as gravure printing is employed, a heat-shrinkable film layer is dissolved or deteriorated with a solvent in ink, the film layer is difficult to have a sufficiently high whiteness and requires higher cost.

#### 【0024】

Each of the front layer 1, the core layer 2, and the back layer 3 constituting the heat-shrinkable opaque white film 4 may further comprise any of additives according to necessity. Such additives include lubricants, fillers, thermostabilizers, antioxidants, ultraviolet absorbents, antistatics, and flame-retarders.



**【0025】**

The thickness of the heat-shrinkable opaque white film 4 can be set as appropriate within ranges not adversely affecting properties such as handleability, appearance, imperviousness to light, and heat-shrinkability. It is, for example, about 10 to about 200  $\mu\text{m}$ , and preferably about 30 to about 70  $\mu\text{m}$ . The thickness of the core layer 2 is generally about 1% to about 80%, preferably about 5% to about 50% of the total thickness of the heat-shrinkable opaque white film 4.

**【0026】**

The heat-shrinkable opaque white film 4 can be prepared according to a conventional procedure for preparing multilayer films, such as coextrusion and lamination. More specifically, a heat-shrinkable opaque white film having the layer configuration (1), i.e., white heat-shrinkable film layer (front layer)/black chromatic heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer), can be prepared by subjecting a resin composition (A) containing a resin and a white colorant, a resin composition (B) containing a resin and a black colorant, and a resin composition (C) containing a resin and a white colorant to melt-coextrusion using an extruder equipped with a T-die or annular die, cooling the extrudate typically using a chill roll, and drawing the cooled extrudate. Drawing can be carried out according to any of tenter drawing and tube drawing. Drawing can be any of biaxial drawing and uniaxial drawing (uniaxial stretching). The percent of stretch can be set as appropriate according to a desired heat-shrinkage percentage. This method comprising the steps of molding a film by coextrusion and drawing the molded film is preferred, because a multilayer film can be easily obtained and the individual layers can be drawn under the same conditions.

**【0027】**

Another heat-shrinkable opaque white film having the layer configuration (1) can be prepared by preparing individual heat-shrinkable films for individual layers by extruding in different steps, and laminating the individual films by dry lamination. According to this method, films comprising resins that are resistant to coextrusion can be laminated, although the resulting multilayer film has adhesive layers between the individual layers and thereby has lower shrinkability than that in the film of coextruded layers.

**【0028】**

A heat-shrinkable opaque white film having the layer configuration (2), i.e., white heat-shrinkable film layer (front layer)/black heat-shrinkable film layer (core layer)/white preprinted layer (back layer), can be produced, for example, by subjecting a resin composition (A) containing a resin and a white colorant, and a resin composition (B) containing a resin and a black colorant to melt

coextrusion using an extruder equipped with a T-die or annular die, cooling the extrudate typically with a chill roll, subjecting the cooled extrudate to drawing in the same manner as above, and forming one or more layers of white printing to a back side of the layer formed from the resin composition (B) (corresponding to the core layer) typically by gravure printing with a white ink. When a white preprinted layer is formed as the back layer typically by gravure printing, the sliding property of the surface of the back layer can be increased by adding, for example, a lubricant to the white ink.

**【0029】**

The heat-shrinkage percentage of the heat-shrinkable opaque white film 4 can be set as appropriate according typically to the shape of container to be applied and is generally 15% or more at least in one direction. For example, the heat-shrinkage percentage of a uniaxially stretched film is generally about 20% to about 90%, and preferably about 30% to about 70% in a main drawing direction when the film is immersed in hot water at 90°C for ten seconds. The heat-shrinkage percentage of a biaxially stretched film is generally about 20% to about 90%, and preferably about 30% to about 70% in one direction (e.g., widthwise direction) and is generally about 1% to about 30%, and preferably about 3% to about 15% in the other direction (e.g., lengthwise direction) when the film is immersed in hot water at 90°C for ten seconds.

**【0030】**

When the heat-shrinkable opaque white film 4 according to the present invention has a black layer as the core layer 2, it can have a very low light transmission factor in the ultraviolet and visible-light regions. The light transmission factor, for example, at wavelengths of 200 to 400 nm is generally 3% or less, and preferably 1% or less. The light transmission factor at wavelengths of 400 to 600 nm is generally 5% or less, and 3% or less. The light transmission factor can be adjusted, for example, by adjusting the content of a black colorant or white colorant in the core layer 2 and/or the thickness of the core layer 2.

**【0031】**

The preprinted ink label layer 5 is a layer having, for example, character information such as trade name or design as a result of printing. It can be formed on a surface of the front layer 1 of the heat-shrinkable opaque white film 4 using an ink according to a conventional printing procedure such as gravure printing, flexographic printing, or screen printing. The ink is not specifically limited, can be a suitable ink selected from, for example, solvent-based inks and water-based inks. Each of these inks can be used alone or in combination. The thickness of the preprinted ink label layer can be selected within ranges of, for example, about 0.5 to about 20  $\mu\text{m}$ , and preferably about 1 to about 10  $\mu\text{m}$ . The preprinted ink label layer can comprise a single layer or plural layers. An overcoat layer

can be arranged on the surface of the preprinted ink label layer typically for protecting the preprinted ink label layer. The surface (inside surface with respect to the container) of the back layer 3 may be subjected to printing and indication typically of characters or may have a sliding coat layer using a transparent ink.

**【0032】**

The shrink label according to the present invention can be formed into a tubular or cylindrical shrink label, for example, by forming the preprinted ink label layer 5 on a surface of the front layer 1 of the heat-shrinkable opaque white film 4, cutting the resulting article to a long slit with a desired width, rolling the cut article into a cylinder so that the preprinted ink label layer 5 faces outward and the main drawing direction is a peripheral direction, sticking the both ends typically with an adhesive or a solvent, or by heat sealing, and cutting the article to a desired length.

**【0033】**

The labeled container according to the present invention comprises a container body and the shrink label according to the present invention applied on or above the container body. The container body is not specifically limited, as long as it is formed from a light-transmittable material. It can be any article such as plastic bottles and glass bottles. Examples of materials for the plastic bottles are thermoplastic resins that can undergo blow molding, including polyester resins such as poly(ethylene terephthalate)s and poly(ethylene naphthalate)s; polystyrene resins such as polystyrenes; polyolefin resins such as polyethylenes and polypropylenes; poly(vinyl chloride)s; polycarbonates; and arylate resins. Each of these materials can be used alone or in combination.

**【0034】**

The labeled container according to the present invention can be produced, for example, by supplying the tubular shrink label to an automatic labeling apparatus, cutting the label to a desired length according to necessity, allowing the label to fit over an article to be applied (container body) continuously, and subjecting the same to heat shrinkage by allowing the same to pass through a steam tunnel or hot-air tunnel at a predetermined temperature. The contents such as beverages can be charged into the container before or after the shrink wrapping.

**【0035】**

The labeled container according to the present invention is suitable, for example, as containers for beverages that are susceptible to discoloration and deterioration caused by light, including alcoholic beverages such as beer, sake, and wine, milk, milky drinks, green tea, and beverages containing vitamins. The labeled container is specifically preferably used as containers for white or pale color (e.g., pale yellow) contents, such as milk or milky drinks, as the back layer of the label is

white.

【0036】

The heat-shrinkable opaque white film according to the present invention has a core layer of black color, can have sufficient imperviousness to light. It has a white front layer, on which an indication print such as of a design can be formed clearly. In addition, when a shrink label using the heat-shrinkable opaque white film is applied to a container, the film has a white back layer, thereby enables clear and sharp looking of the contents and yields excellent appearance of the contents.

【0037】

(Examples)

The present invention will be illustrated in further detail with reference to several examples below which by no means limit the scope of the present invention.

【0038】

< HEAT-SHRINKABLE TRANSLUCENT WHITE FILM, SHRINK LABEL AND CONTAINER WITH LABEL >

[Example 1]

A polystyrene resin composition [(titanium dioxide)/(polystyrene resin) (weight ratio) = 5/95] for forming back and front layers was prepared by blending a styrene-conjugated diene block copolymer [a product of Denki Kagaku Kogyo Kabushiki Kaisha under the trade name of "CLEAREN 530L"] with a polystyrene (GPPS) [a product of SUMIKA COLOR CO., LTD. under the trade name of "SPSM-7G971"] master batch containing 60 percent by weight of titanium dioxide ( $\text{TiO}_2$ ). A polystyrene resin composition [(carbon black)/(polystyrene resin) (weight ratio) = 1/99] for forming a core layer was prepared by blending a styrene-conjugated diene block copolymer [a product of Denki Kagaku Kogyo Kabushiki Kaisha under the trade name of "CLEAREN 530L"] with a polystyrene (GPPS) [a product of SUMIKA COLOR CO., LTD. under the trade name of "SPAB-851"] master batch containing 40 percent by weight of carbon black. These resin compositions were fed to an extruder equipped with a T-die and were coextruded at a temperature of 220°C, the extrudate was cooled with a chill roll and was drawn 1.2 times in a lengthwise direction and 4 times in a widthwise direction to yield a long heat-shrinkable film. This film has a three-layer configuration and has a thickness of 50  $\mu\text{m}$  (ratio of thickness of layers: (front layer)/(core layer)/(back layer) = 4/3/4).

Design print and transparent overcoat were applied to one side (a surface of the front layer) of the long heat-shrinkable film using a gravure printing machine to thereby yield a shrink label. The shrink label was slit in a lengthwise direction to a predetermined length to yield plural rolls. Each roll was rewound, was rolled so that the designed surface is outside and the widthwise direction of the

film is a peripheral direction, the both ends of which were adhered with each other and thereby yielded a long tube. This was cut to an appropriate length and thereby yielded a tubular shrink label. The tubular shrink label was allowed to fit for the body of a PET bottle containing milk and having an inner capacity of 280 ml and was shrunk by passing through a steam tunnel. Thus, a labeled container was produced.

【0039】

[Example 2]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a polystyrene resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/(polystyrene resin) (weight ratio) of 2/98. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0040】

[Example 3]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a polystyrene resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/(polystyrene resin) (weight ratio) of 5/95. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0041】

[Example 4]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a polystyrene resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/(polystyrene resin) (weight ratio) of 10/90. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0042】

[Comparative Examples 1]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a polystyrene resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/(polystyrene resin) (weight ratio) of 0/100. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0043】

[Comparative Examples 2]

A heat-shrinkable film having a two-layer configuration was prepared by the procedure of EXAMPLE 1, except for forming a back layer. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0044】

[Example 5]

A poly(ethylene terephthalate) resin composition for forming back and front layers [(titanium dioxide)/(PET resin) (weight ratio) = 5/95] was prepared by blending a poly(ethylene terephthalate) resin (PET resin) [a product of Eastman Chemical Company under the trade name of "Embrace"] with a PET resin [a product of SUMIKA COLOR CO., LTD. under the trade name of "EPM-7670"] white master batch containing 50 percent by weight of titanium dioxide ( $\text{TiO}_2$ ). Separately, a poly(ethylene terephthalate) resin composition for forming a core layer [(titanium dioxide)/(PET resin) (weight ratio) = 1/99 was prepared by blending a PET resin [a product of Eastman Chemical Company under the trade name of "Embrace"] with a PET resin [a product of SUMIKA COLOR CO., LTD. under the trade name of "EPM-8400"] master batch containing 30 percent by weight of carbon black. These resin compositions were fed to an extruder equipped with a T-die, were coextruded at a temperature of 250°C, the extrudate was cooled with a chill roll, was drawn 4.5 times in a widthwise direction and thereby yielded a long heat-shrinkable film having a three-layer configuration and having a thickness of 50  $\mu\text{m}$  (ratio of thickness of layers: (front layer)/(core layer)/(back layer) = 4/3/4).

Design print and transparent overcoat were applied to one side (a surface of the front layer) of the long heat-shrinkable film using a gravure printing machine to thereby yield a shrink label. The shrink label was slit in a lengthwise direction to a predetermined length to yield plural rolls. Each roll was rewound, was rolled so that the designed surface is outside and the widthwise direction of the film is a peripheral direction, the both ends of which were adhered with each other and thereby yielded a long tube. This was cut to an appropriate length and thereby yielded a tubular shrink label. The tubular shrink label was allowed to fit for the body of a PET bottle containing milk and having an inner capacity of 280 ml and was shrunk by passing through a steam tunnel. Thus, a labeled container was produced.

【0045】

[Example 6]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 5, except for using a poly(ethylene terephthalate) resin composition for forming a core

layer having a compositional ratio (by weight) of (carbon black)/( PET resin) (weight ratio) of 2/98. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 5.

【0046】

[Example 7]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 5, except for using a poly(ethylene terephthalate) resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/( PET resin) (weight ratio) of 5/95. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 5.

【0047】

[Example 8]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 5, except for using a poly(ethylene terephthalate) resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/( PET resin) (weight ratio) of 10/90. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 5.

【0048】

[Comparative Examples 3]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 5, except for using a poly(ethylene terephthalate) resin composition for forming a core layer having a compositional ratio (by weight) of (carbon black)/( PET resin) (weight ratio) of 0/100. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 5.

【0049】

[Comparative Examples 4]

A heat-shrinkable film having a two-layer configuration was prepared by the procedure of EXAMPLE 5, except for forming a back layer. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 5.

【0050】

Evaluation Test

The heat-shrinkable films prepared according to the examples and comparative examples were subjected to the following evaluation test. The results are shown in Table 1 and 2. In Table 1, "PS",

and "PET" represent a polystyrene resin, and a poly(ethylene terephthalate) resin, respectively. The "front", "core", and "back" in the film composition represent resin compositions constituting the front layer, core layer, and back layer, respectively.

**【0051】**

(Imperviousness to light)

The light transmission factor at wavelengths of 200 to 800 nm of each of the heat-shrinkable films prepared according to the examples and comparative examples was determined using a near-infrared-ultraviolet-visible spectrophotometer [a product of Shimadzu Corporation under the trade name of "UV-3101PC"], and the imperviousness to light was evaluated according to the following criteria.

FIG. 2 shows the measurements of the light transmission factor of the heat-shrinkable films prepared according to EXAMPLE 2, 3, and 4, and COMPARATIVE EXAMPLE 1, respectively. The symbols a, b, c, and d in FIG. 2 represent the measurements of the heat-shrinkable films according to EXAMPLES 4, 3, and 2, and, respectively.

A: The light transmission factor at wavelengths of 400 to 600 nm is 5% or less.

C: The light transmission factor at wavelengths of 400 to 600 nm is more than 5%.

**【0052】**

(Whiteness)

The whiteness on a surface of the front layer of each of the heat-shrinkable films prepared according to the examples and comparative examples was visually evaluated according to the following criteria,

A: each have a white surface with a sharp design, in which a black color of the core layer is substantially trivial

B: each have a surface of slightly grayish white but with a sharp design

C: each have a surface with a blackish grey, and with a dark design

**【0053】**

(Heat-shrinkage percentage)

The test specimen of each of the heat-shrinkable film prepared according to the examples and comparative examples was cut into the size of 10cm x 10cm (length of widthwise direction x length of lengthwise direction). The heat-shrinkage percentage was obtained according to measuring length of widthwise direction of the film after the test specimen was immersed in hot water at 90°C for ten seconds.

**【0054】**



## (Appearance of contents)

The contents (milk) was viewed through a spout of the labeled containers produced according to the examples and comparative examples, and the appearance of the contents was visually evaluated according to the following criteria.

A: The milk looks white and fresh.

C: The milk looks black.

【0055】

【Table 1】

Table 1

		Example				Comparative Example	
		1	2	3	4	1	2
Front layer (%)	PS	95	95	95	95	95	95
	TiO <sub>2</sub>	5	5	5	5	5	5
Core layer (%)	PS	99	98	95	90	100	95
	CB	1	2	5	10	0	5
Film configuration		front/core/back		front/core/back		front/core	
Imperviousness to light		A	A	A	A	C	A
Whiteness		A	A	A	B	A	A
Heat shrinkage (%)		53	53	51	48	55	51
Appearance of contents		A	A	A	A	A	C

【0056】

【Table 2】

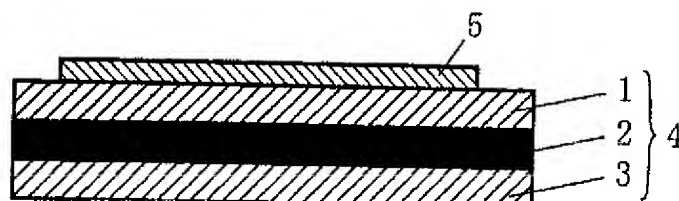
Table 2

		Example				Comparative Example	
		5	6	7	8	3	4
Front layer (%)	PS	95	95	95	95	95	95
	TiO <sub>2</sub>	5	5	5	5	5	5
Core layer (%)	PS	99	98	95	90	100	95
	CB	1	2	5	10	0	5
Film configuration		front/core/back		front/core/back		front/core	
Imperviousness to light		A	A	A	A	C	A
Whiteness		A	A	A	B	A	A
Heat shrinkage (%)		71	69	68	67	71	69
Appearance of contents		A	A	A	A	A	C

(Brief description of drawing)

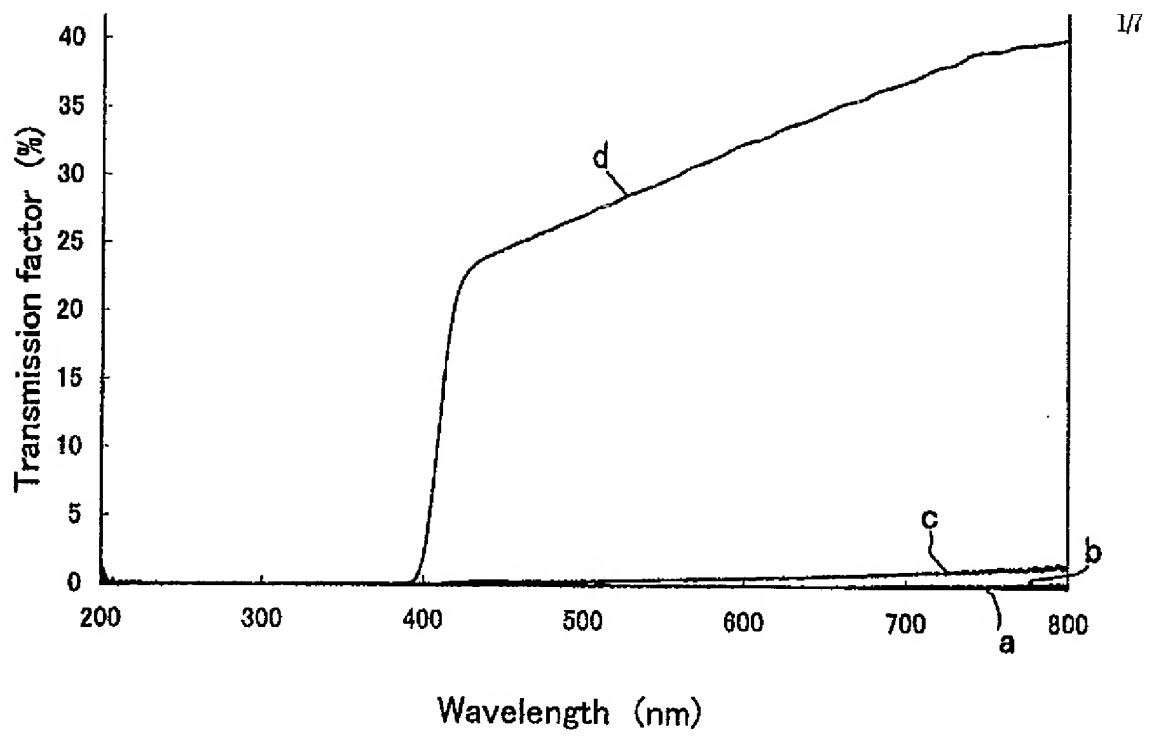
【Fig.1】

FIG. 1 is a schematic cross-sectional view showing an example of the shrink label according to the present invention.



【Fig.2】

FIG. 2 is a graph showing light transmission factors (transmittances) of heat-shrinkable films obtained according to EXAMPLES 2, 3, and 4, and Comparative Examples 1.



(Explanation of letters or numerals)

1: a front layer

2: a core layer

3: a back layer

4: a heat-shrinkable translucent white film

5: a preprinted ink label layer

DECLARATION

I, Mizuho UTAFUSA, a subject of Japan residing at 1192, Noguwa ,  
Kamigori-cho, Ako-gun, Hyogo 678-1202, Japan, solemnly and sincerely  
declare:

That I have a thorough knowledge of the Japanese and English  
languages; and

That the attached pages contain a correct translation into  
English of the priority document of Japanese Patent Application No.  
284765/2003.

Signed this 1st day of July, 2008

歌房みずほ

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Mizuho UTAFUSA

【Document】 Request for Patent  
【Docket No.】 P03FS013  
【Date of Application】 August 2, 2003  
【Address】 Commissioner, Patent Office  
【International Patent Classification】  
B65D25/34  
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【Name】 GOTO Yukihiisa  
【Payment of Fees】  
【Deposit Account No.】 053718  
【Amount to be paid】 21,000  
【Attached Documents】  
【Item】 Claims one copy  
【Item】 Specification one copy  
【Item】 Abstract one copy  
【General Power of Attorney No.】  
0012030

/

**【Document】** Specification

**【Title】** HEAT-SHRINKABLE TRANSLUCENT WHITE FILM, SHRINK LABEL AND CONTAINER WITH LABEL

**【Field of the Invention】**

**【0001】**

The present invention relates to a heat-shrinkable opaque white (translucent white) film which is impervious to light, a shrink label prepared from the heat-shrinkable opaque white film, and a labeled container including a container body and the label applied to the container body by heat shrinkage.

**【Description of the Related Art】**

**【0002】**

Alcoholic beverages such as beer, sake, and wine, green tea, and beverages containing vitamins are susceptible to discoloration and/or deterioration caused by light, in particular light at wavelengths of 380 to 500 nm. Widely used containers typically for beverages susceptible to light-induced deterioration are plastic bottles and glass bottles which are colored for achieving imperviousness to light. These colored containers contain colorants, and this significantly inhibits recovery and reuse of used containers.

**【0003】**

A proposed solution to this is labeled containers including a colorless, transparent plastic bottle or glass bottle as a container body coated with a shrink label having imperviousness to light. Japanese Unexamined Patent Application Publication (JP-A) No. 2002-68202, for example, discloses a bottle having a heat-shrinkable synthetic resin film containing an ultraviolet screening agent such as zinc oxide. JP-A No. 2002-285020 discloses a container with a heat-shrinkable label prepared from a white film containing a specific amount of titanium dioxide. These containers, however, have relatively high light transmission factor particularly to visible light and do not have sufficient imperviousness to light. JP-A No. 2003-26252 discloses a container with a shrink label. The shrink label includes a heat-shrinkable film containing a white pigment and having one side to be designed and the other side printed black. This type of container, however, has a black inner side of the label, and when one look in on a beverage such as milk beverage or beer at an inlet of the container bottle, the beverage looks blackish and has poor appearance which could deteriorate one's appetite.

**【0004】**

**【Document 1】** Japanese Unexamined Patent Application Publication (JP-A) No. 2002-68202

【Document 2】Japanese Unexamined Patent Application Publication (JP-A) No. 2002-285020

【Document 3】 Japanese Unexamined Patent Application Publication (JP-A) No. 2003-26252

【Detailed Description of the Invention】

【Object of the Invention】

【0005】

Accordingly, an object of the present invention is to provide a labeled container that can prevent its contents from discoloration and deterioration caused by light, can be printed clearly typically with a design, and yields an excellent appearance of the contents when viewed from outside. Another object of the present invention is to provide a heat-shrinkable opaque white film and a shrink label which are useful for preparing the labeled container.

【Aspects of the Invention】

【0006】

After intensive investigations to achieve the above objects, the present inventors have found that, by covering a container body with a shrink label using a heat-shrinkable opaque white film having a specific layer configuration, the resulting container can prevent its contents such as beverages from light-induced deterioration, have, for example, a clear design, and show such an excellent appearance of the contents such as beverages that the contents look their original colors without discomfort. The present invention has been achieved based on these findings.

【Advantages in the Invention】

【0007】

Specifically, the present invention provides a heat-shrinkable opaque white film comprising a core layer; and white back and front layers, the core layer having a chromatic color with low transparency to light at wavelengths of 380 to 500 nm or an achromatic color.

【0008】

The core layer may contain at least one of black, yellow, red, and brown pigments. The heat-shrinkable opaque white film has, in a preferred embodiment, a transmission factor to light at wavelengths of 380 to 500 nm of 5% or less.

【0009】

The present invention also provides a shrink label comprising the heat-shrinkable opaque white film, and a preprinted ink label layer arranged on or above a surface of the front layer of the film.

【0010】

The present invention further provides a labeled container comprising a container body; and the shrink label arranged on or above the container body.

#### 【Embodiments】

##### 【0011】

The present invention will be illustrated in detail with reference to the attached drawings according to necessity. The heat-shrinkable opaque white film according to the present invention comprises a core layer (central layer); and white back and front layers (front layer and back layer). The core layer has a chromatic color having low transparency to light (blocking light) at wavelengths of 380 to 500 nm or an achromatic color. The "front layer" means a layer which constitutes an outside layer when applied to a container and is to be printed typically with a design upon the preparation of a label. The "back layer" means a layer lying near to a container when formed into a label. The heat-shrinkable opaque white film according to the present invention can prevent the contents such as a beverage containing vitamins or beer from discoloration and deterioration, since the core layer has an achromatic color or has imperviousness to light at wavelengths of 380 to 500 nm (the ultraviolet region to the blue-green visible light region). A design or such can be clearly printed when the film is formed into a label, since the front layer is white and the film is thereby opaque white. In addition, when the label is applied to a container to form a labeled container, the contents in the container, such as beverages, look natural without deterioration of their original colors when viewed from the spout of the container, since the back layer is white. The heat-shrinkable opaque white film may further comprise any other layer or layers within ranges not adversely affecting the properties such as heat-shrinkability, beauty and handleability, in addition to the core layer and the back and front layers. Examples of the other layers are transparent resin layers, other colored resin layers, and resin layers for improving adhesion between layers,

##### 【0012】

The shrink label according to the present invention comprises the heat-shrinkable opaque white film and a preprinted ink label layer arranged on or above a surface of the front layer. FIG. 1 is a schematic cross-sectional view showing an example of the shrink label according to the present invention. The illustrated shrink label comprises a heat-shrinkable opaque white film 4 and a preprinted ink label layer 5. The heat-shrinkable opaque white film 4 comprises a white front layer 1, a core layer 2 having a chromatic color with low transparency to light at wavelengths of 380 to 500 nm or an achromatic color, and a white back layer 3. The preprinted ink label layer 5 is arranged on a surface of the front layer 1 of the film 4.



**【0013】**

Each of the front layer 1, the core layer 2, and the back layer 3 may independently comprise a heat-shrinkable film layer. Materials for such heat-shrinkable film layers can be those generally used as materials for heat-shrinkable films, such as polyester resins, polystyrene resins, polyolefin resins, and poly(vinyl chloride) resins. Each of these materials can be used alone or in combination.

**【0014】**

The polyester resins can be polyester resins prepared according to a conventional procedure such as condensation between a diol component and a dicarboxylic acid component (or a reactive derivative thereof, such as an ester). Examples of the diol component constituting the polyester resins are aliphatic diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, and 2,2,4-trimethyl-1,6-hexanediol; thiodiethanol; polyalkylene glycols such as diethylene glycol, dipropylene glycol, polyethylene glycol, and polypropylene glycol; alicyclic diols such as 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, and 1,4-cyclohexanedimethanol; and aromatic diols including ethylene oxide adducts of bisphenol compounds such as 2,2-bis(4'- $\beta$ -hydroxyethoxydiphenyl)propane and bis(4'- $\beta$ -hydroxyethoxyphenyl)sulfone, as well as xylylene glycol. Each of these diol components can be used alone or in combination.

**【0015】**

Examples of the dicarboxylic acid component constituting the polyester resins are aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid; alicyclic dicarboxylic acids such as 1,4-decahydronaphthalenedicarboxylic acid, 1,5-decahydronaphthalenedicarboxylic acid, 2,6-decahydronaphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, and 1,4-cyclohexanedicarboxylic acid; and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 4,4'-biphenyldicarboxylic acid, trans-3,3'-stilbenedicarboxylic acid, trans-4,4'-stilbenedicarboxylic acid, 4,4'-dibenzoyldicarboxylic acid, and naphthalenedicarboxylic acids such as 2,6-naphthalenedicarboxylic acid. Each of these dicarboxylic acid components can be used alone or in combination.

**【0016】**

Preferred polyester resins are those prepared by using ethylene glycol as a main diol component, and an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, or a

naphthalenedicarboxylic acid as a main dicarboxylic acid component.

**【0017】**

The polystyrene resins can be styrene-conjugated diene block copolymers such as styrene-butadiene-styrene block copolymers and styrene-isoprene-styrene block copolymers; and mixtures of the styrene-conjugated diene block copolymers with one or more other polymers such as polystyrenes or copolymers between styrene and an acrylic monomer such as (meth)acrylic ester. The styrene-conjugated diene block copolymers may each have a styrene content of about 30 to about 95 percent by weight and a conjugated diene content of about 5 to about 70 percent by weight.

**【0018】**

Each of the white front layer 1 and the white back layer 3 can independently comprise the resin component and a white colorant. Such white colorants are not limited and include white pigments such as titanium dioxide, antimony white, zinc sulfide, and zinc white. Among them, titanium dioxide has high whiteness to prevent the chromatic color of the core layer 2 from being seen through and is particularly preferred. The content of the white colorant in each of the front layer 1 and the back layer 3 can be set as appropriate according typically to the whiteness and cost and varies depending on the species of the white colorant. It is generally about 5 to about 30 percent by weight, and preferably about 6 to about 15 percent by weight of the total weight of each layer.

**【0019】**

The average particle diameter of a white pigment such as titanium dioxide, if used as the white colorant, is, for example, about 0.01 to about 1  $\mu\text{m}$ , preferably about 0.1 to about 0.5  $\mu\text{m}$ . If the average particle diameter is less than 0.01  $\mu\text{m}$ , dispersibility may be deteriorated. If it exceeds 1  $\mu\text{m}$ , the film may have a rough surface and show a deteriorated appearance.

**【0020】**

Adding a small amount of blue colorant such as a blue pigment to the white front layer 1 makes a yellow, red or brown color of the core layer become inconspicuous when viewed from the front side. The amount of the blue colorant is, for example, about 0.01 to about 0.5 percent by weight based on the total weight of the front layer 1.

**【0021】**

The core layer 2 can comprise the resin component and a chromatic colorant which is capable of preventing light (is impervious to light) at wavelengths of 380 to 500 nm from passing through. The chromatic colorant can be, for example, any of yellow pigments, red pigments, and

brown pigments. Examples of the yellow pigments are inorganic pigments such as yellow ocher, aureolin, cadmium yellow, cadmium orange, chromium yellow, zinc yellow, Naples yellow, and nickel yellow; and organic pigments such as azo pigments and greenish yellow. Examples of the red pigments are inorganic pigments such as cadmium red, cadmopone red, chromium red, vermilion, and iron oxide red; and organic pigments such as azo pigments, alizarin lake, quinacridone, and cochineal lake perylene. The brown pigments include inorganic pigments such as umber, raw umber, burnt umber, yellow ocher, Vandyke brown, sienna, raw sienna, burnt sienna, and iron oxide red; and organic pigments such as sepia. Each of these chromatic colorants can be used alone or in combination.

#### 【0022】

The content of the chromatic colorant in the core layer 2 can be set as appropriate in consideration typically of the imperviousness to light (light blocking property) and cost within ranges not adversely affecting the whiteness of the back and front layers of the film. It is generally about 0.1 to about 20 percent by weight, and preferably about 0.5 to about 15 percent by weight based on the total weight of the core layer 2. The amount of the chromatic colorant is preferably 0.05 percent by weight or more (e.g., about 0.05 to about 5 percent by weight) based on the total weight of the heat-shrinkable opaque white film. The content of the chromatic colorant per unit area of the opaque white film is preferably about  $5 \times 10^{-5} \text{ g/m}^2$  or more (e.g., about  $5 \times 10^{-5} \text{ g/m}^2$  to about  $5 \text{ g/m}^2$ ) and more preferably about  $5 \times 10^{-3} \text{ g/m}^2$  or more (e.g., about  $5 \times 10^{-3} \text{ g/m}^2$  to about  $5 \text{ g/m}^2$ ).

#### 【0023】

While varying depending on its species, the average particle diameter of the chromatic colorant generally about 0.01 to about 1  $\mu\text{m}$ . If the average particle diameter exceeds 1  $\mu\text{m}$ , sufficient imperviousness to light may not be satisfactorily obtained. If it is less than 0.01  $\mu\text{m}$ , the dispersibility may often decrease. When the colorant is a yellow pigment, the average particle diameter is particularly preferably within the range of 0.3 to 0.6  $\mu\text{m}$ . In the case of a brown pigment, the average particle diameter is particularly preferably in the range of 0.4 to 0.7  $\mu\text{m}$ .

#### 【0024】

The core layer 2 may further comprise a white colorant such as a white pigment, for increasing the whiteness. When a red pigment and/or a brown pigment is used as the chromatic colorant, the chromatic color of the core layer 2 may slightly appear on the surface of the film. The chromatic color of the core layer 2 can be substantially fully masked by adding a white colorant to the core layer 2. The white colorant herein can be as mentioned above, of which titanium

dioxide is preferred. The content of the white colorant, if added, is, for example, about 0.1 to about 50 percent by weight, and preferably about 5 to about 20 percent by weight based on the total weight of the core layer 2.

【0025】

In the heat-shrinkable opaque white film 4 according to the present invention, it is not always necessary to constitute all the front layer 1, the core layer 2 and the back layer 3 as heat-shrinkable film layers, as long as the heat-shrinkable opaque white film as a whole is heat-shrinkable. Heat-shrinkability can be imparted to the opaque white film 4, for example, by constituting one or two of the three layers as heat-shrinkable film layers, or arranging a heat-shrinkable film layer in addition to the three layers. Each of the front layer 1, the core layer 2, and the back layer 3 can comprise a printed layer or a coating layer, if not a heat-shrinkable film layer. The front layer 1 and the back layer 3 can be formed, for example, by printing both sides (back and front sides) of an achromatic or chromatic heat-shrinkable film layer to be the core layer 2 with an ink containing a white pigment such as titanium dioxide according to a conventional printing procedure such as gravure printing. Likewise, the core layer 2 can be formed by printing a white heat-shrinkable film layer to be the front layer 1 with an ink containing an achromatic or chromatic colorant according to a conventional printing procedure such as gravure printing. When the film comprise two or more heat-shrinkable film layers, resins constituting these layers may be of different species but are preferably of the same species from the viewpoints typically of workability and recycling property.

【0026】

Representative layer configurations of the heat-shrinkable opaque white film 4 include (1) white heat-shrinkable film layer (front layer)/chromatic heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer); (2) white heat-shrinkable film layer (front layer)/chromatic heat-shrinkable film layer (core layer)/white preprinted layer (back layer); and (3) white preprinted layer (front layer)/chromatic heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer). Preferred layer configurations in the present invention are those in which at least the core layer 2 is a chromatic heat-shrinkable film layer. In these layer configurations, cost can be reduced. This is because, for example, a sufficient density can be achieved by directly kneading a chromatic colorant into a resin. It is preferred to constitute all the front layer 1, the core layer 2, and the back layer 3 as heat-shrinkable film layers. This is because, for example, (i) the three layers can be formed by an easy and convenient procedure of coextrusion, heat-shrinkability can be imparted by subjecting the extruded three layers to drawing simultaneously, and the heat-shrinkable

opaque white film can thereby be produced with high production efficiency; (ii) if a printing process such as gravure printing is employed, a heat-shrinkable film layer is dissolved or deteriorated with a solvent in ink, the film layer is difficult to have a sufficiently high whiteness and requires higher cost; and (iii) when a preprinted layer is highly shrunk, it may have ink cracking and have a deteriorated appearance.

**【0027】**

Each of the front layer 1, the core layer 2, and the back layer 3 constituting the heat-shrinkable opaque white film 4 may further comprise any of additives according to necessity. Such additives include lubricants, fillers, thermostabilizers, antioxidants, ultraviolet absorbents, antistatics, and flame-retarders.

**【0028】**

The thickness of the heat-shrinkable opaque white film 4 can be set as appropriate within ranges not adversely affecting properties such as handleability, appearance, imperviousness to light, and heat-shrinkability. It is, for example, about 10 to about 200  $\mu\text{m}$ , and preferably about 30 to about 70  $\mu\text{m}$ . The thickness of the core layer 2 is generally about 1% to about 80%, preferably about 5% to about 50% of the total thickness of the heat-shrinkable opaque white film 4.

**【0029】**

The heat-shrinkable opaque white film 4 can be prepared according to a conventional procedure for preparing multilayer films, such as coextrusion and lamination. More specifically, a heat-shrinkable opaque white film having the layer configuration (1), i.e., white heat-shrinkable film layer (front layer)/chromatic heat-shrinkable film layer (core layer)/white heat-shrinkable film layer (back layer), can be prepared by subjecting a resin composition (A) containing a resin and a white colorant, a resin composition (B) containing a resin and a chromatic colorant, and a resin composition (C) containing a resin and a white colorant to melt-coextrusion using an extruder equipped with a T-die or annular die, cooling the extrudate typically using a chill roll, and drawing the cooled extrudate. Drawing can be carried out according to any of tenter drawing and tube drawing. Drawing can be any of biaxial drawing and uniaxial drawing (uniaxial stretching). The percent of stretch can be set as appropriate according to a desired heat-shrinkage percentage. This method comprising the steps of molding a film by coextrusion and drawing the molded film is preferred, because a multilayer film can be easily obtained and the individual layers can be drawn under the same conditions.

**【0030】**

Another heat-shrinkable opaque white film having the layer configuration (1) can be

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prepared by preparing individual heat-shrinkable films for individual layers by extruding in different steps, and laminating the individual films by dry lamination. According to this method, films comprising resins that are resistant to coextrusion can be laminated, although the resulting multilayer film has adhesive layers between the individual layers and thereby has lower shrinkability than that in the film of coextruded layers.

**【0031】**

A heat-shrinkable opaque white film having the layer configuration (2), i.e., white heat-shrinkable film layer (front layer)/chromatic heat-shrinkable film layer (core layer)/white preprinted layer (back layer), can be produced, for example, by subjecting a resin composition (A) containing a resin and a white colorant, and a resin composition (B) containing a resin and a chromatic colorant to melt coextrusion using an extruder equipped with a T-die or annular die, cooling the extrudate typically with a chill roll, subjecting the cooled extrudate to drawing in the same manner as above, and forming one or more layers of white printing to a side of the layer formed from the resin composition (B) (corresponding to the core layer) typically by gravure printing with a white ink. When a white preprinted layer is formed as the back layer typically by gravure printing, the sliding property of the surface of the back layer can be increased by adding, for example, a lubricant to the white ink.

**【0032】**

The heat-shrinkage percentage of the heat-shrinkable opaque white film 4 can be set as appropriate according typically to the shape of container to be applied and is generally 15% or more at least in one direction. For example, the heat-shrinkage percentage of a uniaxially stretched film is generally about 20% to about 90%, and preferably about 30% to about 70% in a main drawing direction when the film is immersed in hot water at 90°C for ten seconds. The heat-shrinkage percentage of a biaxially stretched film is generally about 20% to about 90%, and preferably about 30% to about 70% in one direction (e.g., widthwise direction) and is generally about 1% to about 30%, and preferably about 3% to about 15% in the other direction (e.g., lengthwise direction) when the film is immersed in hot water at 90°C for ten seconds.

**【0033】**

When the heat-shrinkable opaque white film 4 according to the present invention has a layer of a chromatic color with low transparency to light at wavelengths of 380 to 500 nm as the core layer 2, the film can have a very low light transmission factor in the ultraviolet and blue-green visible-light regions. The light transmission factor at wavelengths of 380 to 500 nm is, for example, 5% or less, and preferably 3% or less. This light transmission factor can be adjusted by

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controlling the content of a yellow, red or brown colorant in the core layer 2 and/or the thickness of the core layer 2.

**【0034】**

The preprinted ink label layer 5 is a layer having, for example, character information such as trade name or design as a result of printing. It can be formed on a surface of the front layer 1 of the heat-shrinkable opaque white film 4 using an ink according to a conventional printing procedure such as gravure printing, flexographic printing, or screen printing. The ink is not specifically limited, can be a suitable ink selected from, for example, solvent-based inks and water-based inks. Each of these inks can be used alone or in combination. The thickness of the preprinted ink label layer can be selected within ranges of, for example, about 0.5 to about 20  $\mu\text{m}$ , and preferably about 1 to about 10  $\mu\text{m}$ . The preprinted ink label layer can comprise a single layer or plural layers. An overcoat layer can be arranged on the surface of the preprinted ink label layer typically for protecting the preprinted ink label layer. The surface (inside surface with respect to the container) of the back layer 3 may be subjected to printing and indication typically of characters or may have a sliding coat layer using a transparent ink.

**【0035】**

The shrink label according to the present invention can be formed into a tubular or cylindrical shrink label, for example, by forming the preprinted ink label layer 5 on a surface of the front layer 1 of the heat-shrinkable opaque white film 4, cutting the resulting article to a long slit with a desired width, rolling the cut article into a cylinder so that the preprinted ink label layer 5 faces outward and the main drawing direction is a peripheral direction, sticking the both ends typically with an adhesive or a solvent, or by heat sealing, and cutting the article to a desired length.

**【0036】**

The labeled container according to the present invention comprises a container body and the shrink label according to the present invention applied on or above the container body. The container body is not specifically limited, as long as it is formed from a light-transmittable material. It can be any article such as plastic bottles and glass bottles. Examples of materials for the plastic bottles are thermoplastic resins that can undergo blow molding, including polyester resins such as poly(ethylene terephthalate)s and poly(ethylene naphthalate)s; polystyrene resins such as polystyrenes; polyolefin resins such as polyethylenes and polypropylenes; poly(vinyl chloride)s; polycarbonates; and arylate resins. Each of these materials can be used alone or in combination.

**【0037】**

The labeled container according to the present invention can be produced, for example, by

supplying the tubular shrink label to an automatic labeling apparatus, cutting the label to a desired length according to necessity, allowing the label to fit over an article to be applied (container body) continuously, and subjecting the same to heat shrinkage by allowing the same to pass through a steam tunnel or hot-air tunnel at a predetermined temperature. The contents such as beverages can be charged into the container before or after the shrink wrapping.

【0038】

The labeled container according to the present invention is suitable, for example, as containers for beverages that are susceptible to discoloration and deterioration caused by light, including alcoholic beverages such as beer, sake, and wine, milk, milky drinks, green tea, and beverages containing vitamins. The labeled container is specifically preferably used as containers for white or pale color (e.g., pale yellow) contents, such as milk or milky drinks, as the back layer of the label is white.

【0039】

(Examples)

The present invention will be illustrated in further detail with reference to several examples below which by no means limit the scope of the present invention.

【0040】

< HEAT-SHRINKABLE TRANSLUCENT WHITE FILM, SHRINK LABEL AND CONTAINER WITH LABEL >

[Example 1]

A polystyrene resin composition for forming back and front layers [(titanium dioxide)/(polystyrene resin) (weight ratio) = 10/90] was prepared by blending a styrene-conjugated diene block copolymer [a product of Denki Kagaku Kogyo Kabushiki Kaisha under the trade name of "CLEAREN 530L"] with a polystyrene (GPPS) [a product of SUMIKA COLOR CO., LTD. under the trade name of "SPSM-7G971"] master batch containing 60 percent by weight of titanium dioxide (TiO<sub>2</sub>). Separately, a polystyrene resin composition for forming a core layer [(red pigment)/(polystyrene resin) (weight ratio) = 0.5/99.5] was prepared by adding to a styrene-conjugated diene block copolymer [a product of Denki Kagaku Kogyo Kabushiki Kaisha under the trade name of "CLEAREN 530L"] 0.5 percent by weight of liquid paraffin as a spreader, and then adding a red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment (azo pigment)] thereto. These resin compositions were fed to an extruder equipped with a T-die and were coextruded at a temperature of 220°C, the extrudate was cooled with a chill roll and was drawn 1.2 times in a lengthwise direction and 4 times in a



widthwise direction to yield a long heat-shrinkable film. This film has a three-layer configuration and has a thickness of 50  $\mu\text{m}$  (ratio of thickness of layers: (front layer)/(core layer)/(back layer) = 2/1/2).

Design print and transparent overcoat were applied to one side (a surface of the front layer) of the long heat-shrinkable film using a gravure printing machine to thereby yield a shrink label. The shrink label was slit in a lengthwise direction to a predetermined length to yield plural rolls. Each roll was rewound, was rolled so that the designed surface is outside and the widthwise direction of the film is a peripheral direction, the both ends of which were adhered with each other and thereby yielded a long tube. This was cut to an appropriate length and thereby yielded a tubular shrink label. The tubular shrink label was allowed to fit for the body of a PET bottle containing milk and having an inner capacity of 280 ml and was shrunk by passing through a steam tunnel. Thus, a labeled container was produced.

#### 【0041】

##### [Example 2]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a yellow pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-347", an inorganic pigment (chromium yellow)] instead of the red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment] to thereby prepare a polystyrene resin composition for forming a core layer [(yellow pigment)/(polystyrene resin) (weight ratio) = 1.0/99.0]. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

#### 【0042】

##### [Example 3]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a brown pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-918", an inorganic pigment (iron oxide red)] instead of the red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment] to thereby prepare a polystyrene resin composition for forming a core layer [(brown pigment)/(polystyrene resin) (weight ratio) = 1.0/99.0]. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

#### 【0043】

##### [Examples 4]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of

EXAMPLE 1, except for using a white pigment [titanium dioxide ( $\text{TiO}_2$ )] in addition to the red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment] to thereby prepare a polystyrene resin composition for forming a core layer [(red pigment)/(white pigment)/(polystyrene resin) (weight ratio) = 0.5/5.0/94.5]. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0044】

[Examples 5]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for using a brown pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-918", an inorganic pigment (iron oxide red)] and a white pigment [titanium dioxide ( $\text{TiO}_2$ )] instead of the red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment] to thereby yield a polystyrene resin composition for forming a core layer [(brown pigment)/(white pigment)/(polystyrene resin) (weight ratio) = 1.0/5.0/94.0]. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0045】

[Comparative Example 1]

A heat-shrinkable film having a three-layer configuration was prepared by the procedure of EXAMPLE 1, except for preparing a polystyrene resin composition for forming a core layer [(red pigment)/(polystyrene resin) (weight ratio) = 0/100] without using the red pigment [a product of SUMIKA COLOR CO., LTD. under the trade name of "SHPA-102", an organic pigment]. Using this heat-shrinkable film, a shrink label and a labeled container were produced by the procedure of EXAMPLE 1.

【0046】

Evaluation Test

The heat-shrinkable films prepared according to the examples and comparative examples were subjected to the following evaluation test. The results are shown in Table 1. In Table 1, "PS", "CB", " $\text{TiO}_2$ ", and "PET" represent a polystyrene resin, carbon black, titanium dioxide, and a poly(ethylene terephthalate) resin, respectively. The "front", "core", and "back" in the film composition represent resin compositions constituting the front layer, core layer, and back layer, respectively. The numerical values in Table 1 are percentages.

【0047】

(Imperviousness to light)

The light transmission factor at wavelengths of 200 to 1000 nm of each of the heat-shrinkable films prepared according to the examples and comparative examples was determined using a near-infrared-ultraviolet-visible spectrophotometer [a product of Shimadzu Corporation under the trade name of "UV-3101PC"], and the imperviousness to light at specific wavelength (380 to 500 nm) was evaluated according to the following criteria.

FIG. 2 shows the measurements of the light transmission factor of the heat-shrinkable films prepared according to COMPARATIVE EXAMPLE 1, and EXAMPLES 1, 2, 3, 4, and 5, respectively. The symbols a, b, c, d, e, and f in FIG. 2 represent the measurements of the heat-shrinkable films according to COMPARATIVE EXAMPLE 1, and EXAMPLES 1, 2, 3, 4 and 5, respectively.

A: The light transmission factor at wavelengths of 380 to 500 nm is 5% or less.

C: The light transmission factor at wavelengths of 380 to 500 nm is more than 5%.

【0048】

(Whiteness)

The whiteness on a surface of the front layer of each of the heat-shrinkable films prepared according to the examples and comparative examples was visually evaluated according to the following criteria,

A: each have a white surface with a sharp design, in which a chromatic color of the core layer is substantially trivial

B: each have a surface of a slightly chromatic color but with a sharp design

C: show a surface with a clear chromatic color.

【0049】

(Appearance of contents)

The contents (milk) was viewed through a spout of the labeled containers produced according to the examples and comparative examples, and the appearance of the contents was visually evaluated according to the following criteria.

A: The milk looks white and fresh.

C: The milk looks chromatic.

【0050】

【Table 1】

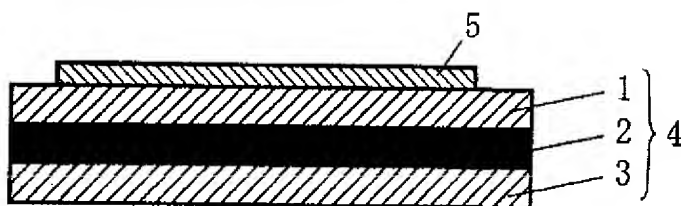
Table 1

		Example					Com. Ex.	
		1	2	3	4	5	1	
Front layer (%)		PS	90	90	90	90	90	90
		TiO <sub>2</sub>	10	10	10	10	10	10
Core layer (%)	PS		99.5	99.0	99.0	94.5	94.0	100
	Pigment	Red	0.5	-	-	0.5	-	-
		Yellow	-	1.0	-	-	-	-
		Brown	-	-	1.0	-	1.0	-
		White	-	-	-	5.0	5.0	-
Film configuration		front/core/back					front/core/back	
Imperviousness to light (numeral in FIG. 2)		A (b)	A (c)	A (d)	A (e)	A (f)	C (a)	
Whiteness		B	A	B	A	A	A	
Appearance of contents		A	A	A	A	A	A	

【0051】

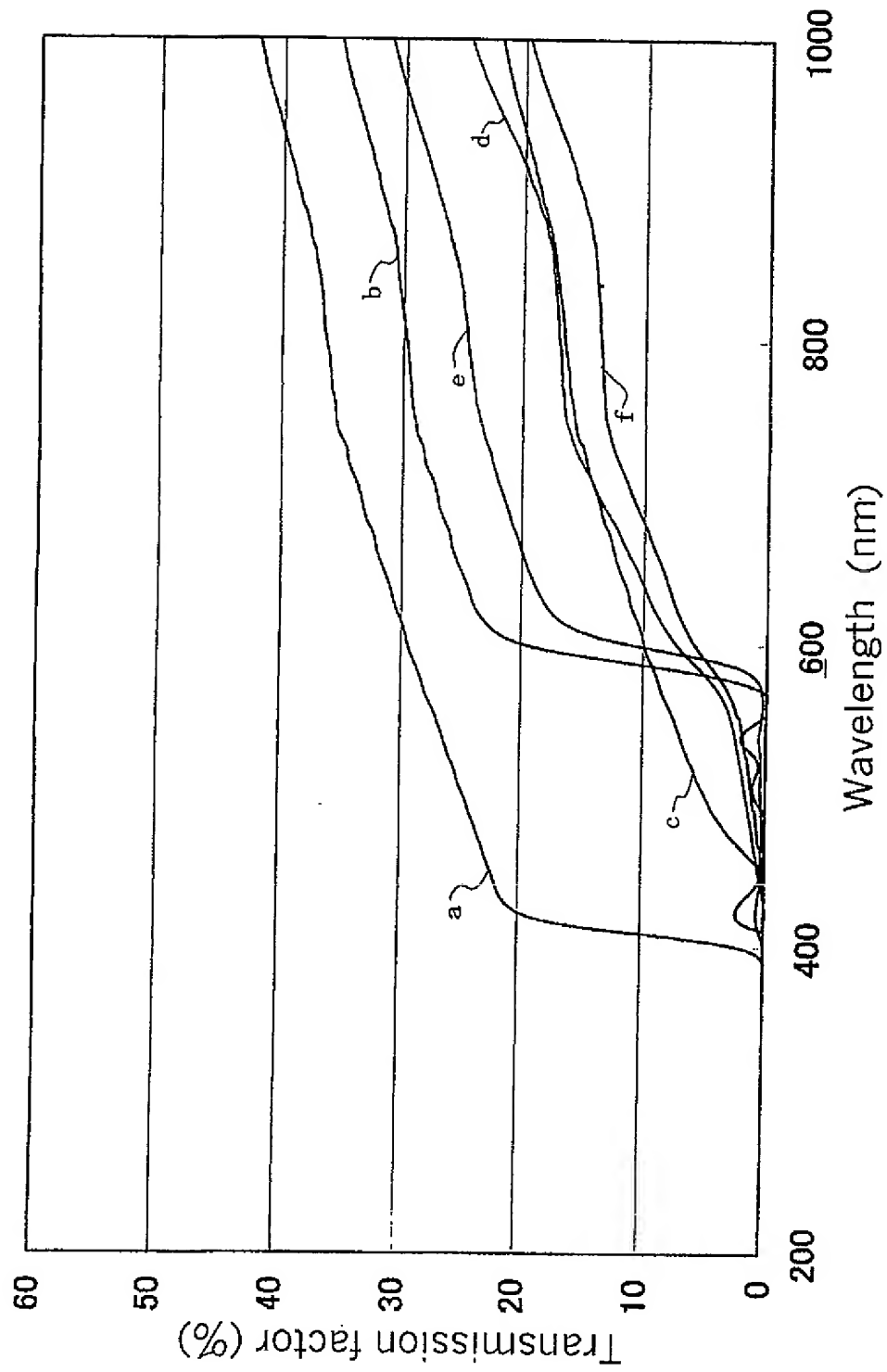
【Fig.1】

FIG. 1 is a schematic cross-sectional view showing an example of the shrink label according to the present invention.



【Fig.2】

FIG. 2 is a graph showing light transmission factors (transmittances) of heat-shrinkable films obtained according to EXAMPLES 1 to 5.



【0052】

(Explanation of letters or numerals)

1: a front layer

2: a core layer

3: a back layer

4: a heat-shrinkable translucent white film